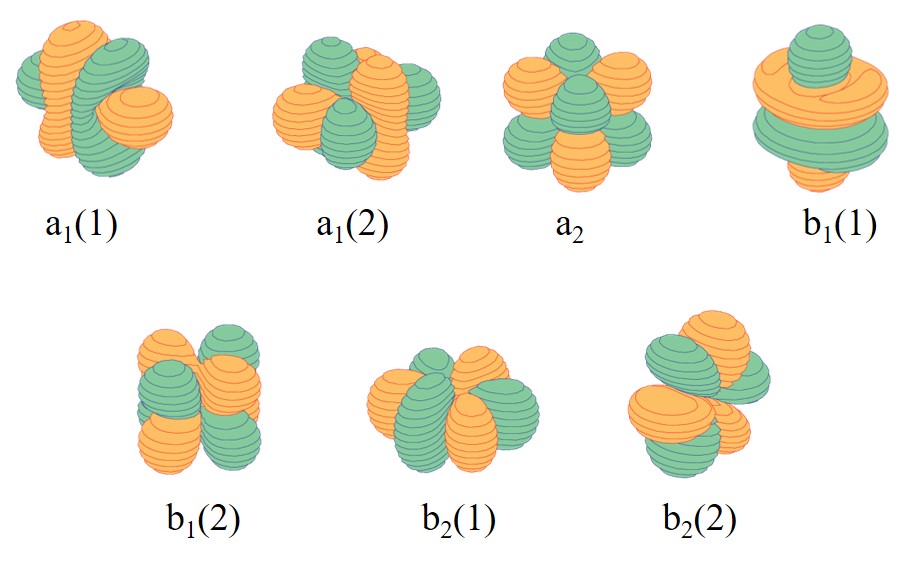
**Supplemental Material**

**Density functional and ab initio study of samarium dihalides, SmX2 (X = I, Br, and Cl)**

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**Figure S1.** The active orbitals of the CAS(6,7) reference wave function of SmI2.

**Table S1.** The relative energies (in kcal/mol) of SmI2 on the optimized molecular structure of the 7B1(2) state by CCSD(T).

|  |  |  |  |
| --- | --- | --- | --- |
| SmI2 | CAS(6,7) | Large frozen core MRCI+Qa | Small frozen core MRCI+Qb |
| 7A1 | 1.76 | 2.12 | 2.11 |
| 7A2(1) | 3.64 | 3.98 | 3.97 |
| 7A2(2) | 0.52 | 0.63 | 0.63 |
| 7B1(1) | 1.76 | 2.00 | 2.00 |
| 7B1(2) | 0.00 | 0.00 | 0.00 |
| 7B2(1) | 3.64 | 3.98 | 3.97 |
| 7B2(2) | 0.64 | 0.74 | 0.74 |

a: the 5s and 5p electrons of Sm and 5s and 5p electrons of I were correlated in the MRCI+Q calculation.

b: the 5s and 5p electrons of Sm and 4d, 5s, and 5p electrons of I were correlated in the MRCI+Q calculation.

**Table S2.** Vibrational frequencies (in cm–1) and NPA charges of low-lying electronic states of SmI2.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| SmI2 | | | PBE0 | B1B95 | B3LYP | MP2 |
| 7A1 | ω | a1 (1)a | 21 | 20 | 22 | 19 |
| a1 (2)b | 134 | 132 | 132 | 139 |
| b2c | 172 | 171 | 167 | 180 |
| NPAd | | 1.337,  -0.669 | 1.349,  -0.674 | 1.342,  -0.671 | 1.317,  -0.658 |
| 7A2(1) | ω | a1 (1)a | 23 | 22 | 24 | 22 |
| a1 (2)b | 137 | 135 | 134 | 143 |
| b2c | 170 | 170 | 166 | 178 |
| NPAd | | 1.324,  -0.662 | 1.337,  -0.669 | 1.327,  -0.664 | 1.301,  -0.651 |
| 7A2(2) | ω | a1 (1)a | 21 | 20 | 22 | 20 |
| a1 (2)b | 134 | 132 | 131 | 140 |
| b2c | 173 | 172 | 168 | 179 |
| NPAd | | 1.342,  -0.671 | 1.353,  -0.676 | 1.347,  -0.674 | 1.313,  -0.656 |
| 7B1(1) | ω | a1 (1)a | 21 | 20 | 22 | 19 |
| a1 (2)b | 134 | 132 | 132 | 139 |
| b2c | 172 | 171 | 167 | 180 |
| NPAd | | 1.337,  -0.668 | 1.348,  -0.674 | 1.341,  -0.671 | 1.317,  -0.658 |
| 7B1(2) | ω | a1 (1)a | 17 | 15 | 18 | 16 |
| a1 (2)b | 130 | 127 | 128 | 136 |
| b2c | 175 | 174 | 170 | 182 |
| NPAd | | 1.353,  -0.677 | 1.367,  -0.684 | 1.356,  -0.678 | 1.330,  -0.665 |
| 7B2(1) | ω | a1 (1)a | 23 | 22 | 24 | 22 |
| a1 (2)b | 137 | 135 | 134 | 143 |
| b2c | 170 | 170 | 166 | 178 |
| NPAd | | 1.324,  -0.662 | 1.337,  -0.669 | 1.327,  -0.663 | 1.301,  -0.650 |
| 7B2(2) | ω | a1 (1)a | 20 | 19 | 21 | 21 |
| a1 (2)b | 133 | 131 | 131 | 142 |
| b2c | 173 | 172 | 168 | 179 |
| NPAd | | 1.340,  -0.670 | 1.352,  -0.676 | 1.342,  -0.671 | 1.306,  -0.653 |

aExperimentally observed vibrational frequency is 26 cm-1 (bending mode) from Ref. [22] in the main text.

bExperimentally observed vibrational frequency is 118 cm-1 (symmetric stretching mode) from Ref. [22] in the main text.

cExperimentally observed vibrational frequency is 168 cm-1 (asymmetric stretching mode) from Ref. [22] in the main text.

dPositive and negative charges are Sm and I atoms of SmI2, respectively.**Table S3.** Vibrational frequencies (in cm–1) and NPA charges of low-lying electronic states of SmBr2.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| SmBr2 | | | PBE0 | B1B95 | B3LYP | MP2 |
| 7A1 | ω | a1 (1)a | 32 | 31 | 32 | 29 |
| a1 (2)b | 183 | 180 | 178 | 191 |
| b2c | 209 | 208 | 203 | 220 |
| NPAd | | 1.427,  -0.713 | 1.439,  -0.720 | 1.431,  -0.715 | 1.422,  -0.711 |
| 7A2(1) | ω | a1 (1)a | 34 | 33 | 35 | 33 |
| a1 (2)b | 184 | 182 | 180 | 193 |
| b2c | 207 | 206 | 202 | 218 |
| NPAd | | 1.415,  -0.707 | 1.429,  -0.714 | 1.416,  -0.708 | 1.409,  -0.705 |
| 7A2(2) | ω | a1 (1)a | 31 | 30 | 31 | 31 |
| a1 (2)b | 182 | 180 | 178 | 192 |
| b2c | 209 | 208 | 204 | 218 |
| NPAd | | 1.431,  -0.716 | 1.443,  -0.721 | 1.437,  -0.718 | 1.418,  -0.709 |
| 7B1(1) | ω | a1 (1)a | 31 | 31 | 31 | 29 |
| a1 (2)b | 183 | 181 | 179 | 191 |
| b2c | 209 | 207 | 203 | 220 |
| NPAd | | 1.426,  -0.713 | 1.439,  -0.719 | 1.430,  -0.715 | 1.423,  -0.711 |
| 7B1(2) | ω | a1 (1)a | 26 | 24 | 27 | 25 |
| a1 (2)b | 179 | 176 | 175 | 188 |
| b2c | 211 | 210 | 206 | 222 |
| NPAd | | 1.442,  -0.721 | 1.456,  -0.728 | 1.445,  -0.722 | 1.436,  -0.718 |
| 7B2(1) | ω | a1 (1)a | 34 | 33 | 34 | 33 |
| a1 (2)b | 184 | 182 | 180 | 193 |
| b2c | 207 | 206 | 202 | 218 |
| NPAd | | 1.415,  -0.707 | 1.428,  -0.714 | 1.416,  -0.708 | 1.409,  -0.704 |
| 7B2(2) | ω | a1 (1)a | 31 | 29 | 31 | 32 |
| a1 (2)b | 182 | 179 | 178 | 193 |
| b2c | 209 | 208 | 204 | 219 |
| NPAd | | 1.430,  -0.715 | 1.443,  -0.722 | 1.432,  -0.716 | 1.413,  -0.707 |

aExperimentally observed vibrational frequency is 40 ± 8 cm-1 (bending mode) from Ref. [23] in the main text.

bExperimentally observed vibrational frequency is 200 ± 10 cm-1 (symmetric stretching mode) from Ref. [23] in the main text.

cExperimentally observed vibrational frequency is 225 ± 10 cm-1 (asymmetric stretching mode) from Ref. [23] in the main text.

dPositive and negative charges are Sm and Br atoms of SmBr2, respectively.

**Table S4.** Vibrational frequencies (in cm–1) and NPA charges of low-lying electronic states of SmCl2.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| SmCl2 | | | PBE0 | B1B95 | B3LYP | MP2 |
| 7A1 | ω | a1 (1)a | 51 | 50 | 51 | 48 |
| a1 (2)b | 282 | 279 | 275 | 291 |
| b2c | 289 | 287 | 282 | 30054 |
| NPAd | | 1.496,  -0.748 | 1.509,  -0.754 | 1.499,  -0.750 | 1.496,  -0.748 |
| 7A2(1) | ω | a1 (1)a | 54 | 52 | 54 | 53 |
| a1 (2)b | 282 | 280 | 275 | 292 |
| b2c | 288 | 285 | 281 | 299 |
| NPAd | | 1.484,  -0.742 | 1.498,  -0.749 | 1.484,  -0.742 | 1.484,  -0.742 |
| 7A2(2) | ω | a1 (1)a | 49 | 48 | 48 | 51 |
| a1 (2)b | 283 | 280 | 276 | 291 |
| b2c | 290 | 287 | 282 | 298 |
| NPAd | | 1.499,  -0.750 | 1.511,  -0.756 | 1.504,  -0.752 | 1.491,  -0.746 |
| 7B1(1) | ω | a1 (1)a | 50 | 48 | 49 | 48 |
| a1 (2)b | 282 | 280 | 275 | 291 |
| b2c | 290 | 287 | 283 | 305 |
| NPAd | | 1.494,  -0.747 | 1.507,  -0.754 | 1.498,  -0.749 | 1.496,  -0.748 |
| 7B1(2) | ω | a1 (1)a | 41 | 37 | 42 | 40 |
| a1 (2)b | 280 | 277 | 274 | 289 |
| b2c | 291 | 288 | 284 | 301 |
| NPAd | | 1.509,  -0.755 | 1.524,  -0.762 | 1.512,  -0.756 | 1.508,  -0.754 |
| 7B2(1) | ω | a1 (1)a | 54 | 52 | 55 | 53 |
| a1 (2)b | 282 | 280 | 275 | 292 |
| b2c | 288 | 285 | 282 | 299 |
| NPAd | | 1.484,  -0.742 | 1.498,  -0.749 | 1.484,  -0.742 | 1.484,  -0.742 |
| 7B2(2) | ω | a1 (1)a | 47 | 46 | 47 | 52 |
| a1 (2)b | 281 | 278 | 274 | 292 |
| b2c | 289 | 286 | 283 | 299 |
| NPAd | | 1.499,  -0.749 | 1.513,  -0.756 | 1.501,  -0.750 | 1.488,  -0.744 |

aBending mode.

bSymmetric stretching mode.

cAsymmetric stretching mode.

dPositive and negative charges are the Sm and Cl atoms of SmCl2, respectively.